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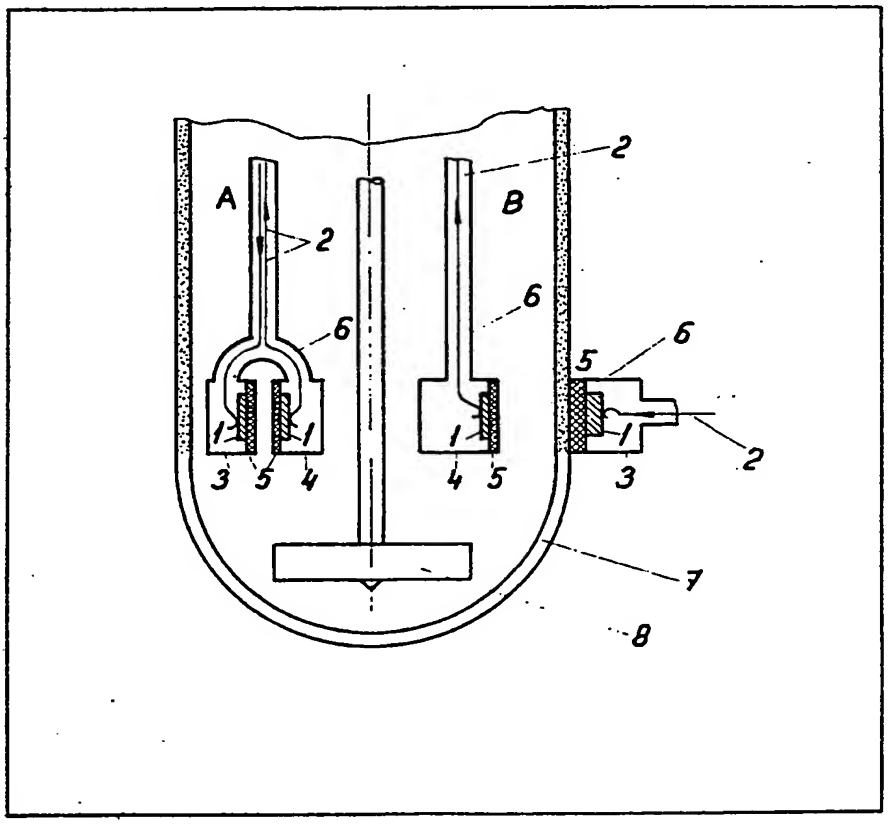
(54) Measuring changes in rheological properties during polymerization

(57) A method of continuously measuring changes in rheological properties of polymers during a polymerization process, wherein longitudinal ultrasonic waves of a frequency from 0.02 to 100 MHz are introduced into the polymerizing system, and their absorption and rate of propagation are measured during the polymerization process. The absorption and rate of propagation of longitudinal ultrasonic waves correlate with the real and imaginary parts of the complex shearing viscosity. In addition, the magnitude of the absorption and rate of propagation of longitudinal ultrasonic waves in dependence on frequency correlate with the mean value of the diameter and with the shape of the particles of the polymerizing system monomer/polymer.



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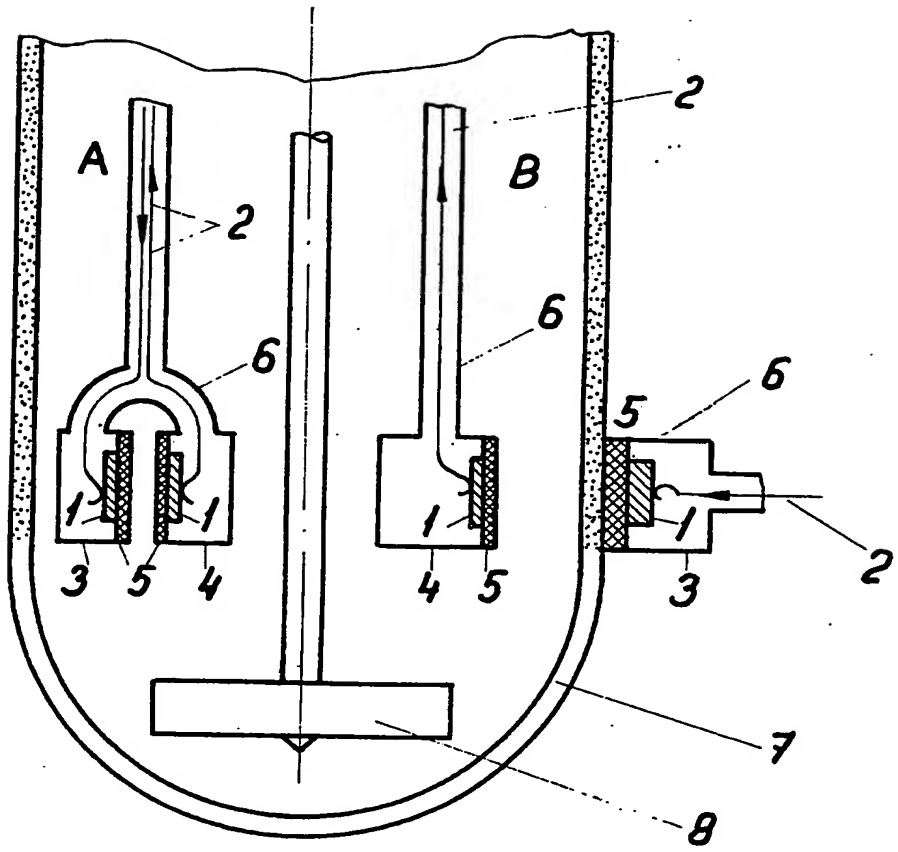

SPECIFICATION

Method and apparatus for continuous measurement of changes in rheological properties of monomers during polymerization

The present invention relates to a method of and apparatus for continuous measurement of changes in the rheological properties of monomers, such as vinyl chloride, during the polymerization process.

During the production of polyvinylchoride, vinyl chloride polymerizes at temperatures ranging from 40 to 80°C, and for this operation there is provided a double-wall reactor provided with a mixing propeller and possibly also with a reflux condenser. In the course of the polymerization process there appear changes in the temperature, pressure, rheological and other physico-chemical quantities; most of these quantities are usually measured, while recorded are the temperature and pressure values of the polymerizing system, together with the cooling water temperature. These quantities, however, provide only incomplete information on the course of the polymerization process, which is of little advantage with regard to their possible application in the feedback control of the process or for the prediction and signallization of the beginning of emergency situations, such as polymerization fouling of the reflux condenser tubes, etc. In order to obtain more complete information on the process of the polymerization of vinyl chloride or other monomers it is therefore desirable to carry out continuous measurement of changes in the rheological properties during the polymerization process.

The current methods and apparatus for the measurement of changes in rheological properties of monomers during polymerization have been based mostly on samples being taken at various stages of the polymerization process, and on visual evaluation of such samples, possibly also on their evaluation by means of other physico-chemical measuring methods.

A disadvantage of these inspection methods and checking apparatus can be seen in the very necessity of taking samples and subsequently evaluating them. The measuring methods used in evaluating the samples taken and in determining the changes in the rheological properties of the polymerizing system are rather complicated and lengthy so that there is a delay in the determination of the values followed. This is of adverse effect especially when the rheological properties of the polymerizing system and those of the sample taken change differently with time. These circumstances make it difficult to intervene immediately into the polymerization process, not to speak of utilizing the values measured for feedback control of the process.

Another considerable disadvantage of the methods based on taking samples is also the fact that they require and are dependent on human attendance.

Also known are low-frequency ultrasonic measuring methods and apparatus which make it possible to measure continuously changes in the viscosity of the polymerizing system during the polymerization process; they work on the principle of scanning the damped oscillations of a metallic waveguide in viscous medium. A drawback of these measuring methods and apparatus lies in that viscosity values can be scanned in this way only in close vicinity to the waveguide which in the first approximation is given by the inverse value of the absorption coefficient of the shearing sound waves of the frequency used. Hence it follows that these types of apparatus are sensitive to polymerization fouling of the surface of the scanning or of the transmitting sonic probe.

It is an object of the present invention to obviate or mitigate the above drawbacks in the methods and apparatus for continuous measuring of changes in rheological properties of monomers during the polymerization process.

According to one aspect of the present invention there is provided a method of continuous measurement of changes in rheological properties of monomers during a polymerization process, comprising introducing into the polymerizing system longitudinal ultrasonic oscillations of a frequency of 0.02 to 100 MHz, with the absorption or the rate of propagation of these oscillations being scanned during the polymerization process.

The quantities measured of the absorption and rate of propagation of longitudinal ultrasonic waves correlate with the real and imaginary parts of the complex shearing viscosity. In addition, the magnitude of the absorption and rate of propagation of longitudinal ultrasonic waves in dependence on frequency correlate with the mean value of the diameter and with the shape of the particles of the polymerizing system monomer/polymer.

The main advantages of the above method consist in that this method offers the possibility of continuously and smoothly measuring during polymerization the rheological volume properties, such as complex viscosity, mean diameter and shape of the particles of the polymerizing system even under flow conditions of the system; it also enables discovering the appearance of local cavitations and of the gaseous phase of the monomer, which lead to the foaming of the system and to polymerization fouling of the reflux condenser. On the basis of spectral dependence of the absorption values or of the rate of propagation of longitudinal ultra-sonic waves measured it is possible to determine optimum parameters at the polymerization process of the individual monomers and to predict the final properties of the polymer.

According to another aspect of the present invention there is provided Apparatus to carry out the method according to claim 1, including at least one ultrasonic transducer which is adapted for both generating and receiving longitudinal ultrasonic waves and which is acoustically coupled with ultrasonic delay lines located in the

polymerizing system.

In the simplest case, the function of both transmitting and receiving ultrasonic wav s is performed by a single ultrasonic transducer arranged for reflection. In this case the reflector is the polymerizing medium itself or possibly the wall of the reaction vessel.

In another variant, the apparatus consists of two ultrasonic transducers, one of which is adapted for generating and the other for receiving longitudinal ultrasonic waves. The two transducers are coupled acoustically with their own delay lines.

In the arrangement with two transducers, i.e. in the throughflow arrangement, two alternatives can again be chosen from: the two ultrasonic transducers are either placed integratedly in the polymerizing monomer or one of them is located in the polymerizing medium while the other is outside the reaction vessel but acoustically coupled with the polymerizing monomer, e.g. by means of the vessel jacket.

With all these alternatives the ultrasonic transducers are with advantage located in holders which together with the delay lines form the pressure and electric insulation jacket of the transducer.

The ultrasonic transducers may be either of the narrow-band or broad-band type; their frequency range is chosen such that the absorption values of longitudinal ultrasonic waves in the polymerizing system do not, in the course of polymerization, xceed the range of the electronic apparatus used.

An advantage of the apparatus according to the invention is, above all, the application of ultrasonic transducers to the generation and reception of longitudinal ultrasonic waves via ultrasonic delay lines, which enables a continuous introduction and scanning of longitudinal ultrasonic oscillations in the polymerizing system and, simultaneously, enable the measuring of absorption and rate of propagation of longitudinal ultrasonic waves with respect to both the throughflow (passage) — when there are two transducers — and reflection — when there is one transducer and a reflector.

With this method the effect is substantially limited of the film of polymer sedimenting at the delay line faces on the magnitude of the quantities measured. The quantities are measured as to their volume, provided the wavelength is at least ten times greater than the thickness of the sedimenting film, and ten times smaller than the distance between the transmitting and the receiving faces of the ultrasonic delay line. The value of the continuously scanned quantity of the absorption coefficient of longitudinal ultrasonic waves can also be used for feedback control of the polymerization process. Even when only current structural materials are used, the method and the apparatus according to the invention make it possible to design equipment which complies with CSN Standards for electric-spark safety and is pressure-resistant in the range from 0.1 to 500 MPa.

An example of the apparatus according to the invention is given in the attached drawing, which shows a v rtical axial section through the polymerizing reactor with double-wall jacket and radial propeller; represented in the left-hand part of the reactor vessel is an embodiment with two integrated ultrasonic transducers (variant "A") while in the right-hand part of the vessel is an alternative embodiment with separate transducers (variant "B").

In the two alternative variants the measuring equipment consists of two ultrasonic transducers *1*; one of which is a transmitting transducer, designed for the generation of longitudinal ultrasonic waves, and the other is a receiving transducer, designed to detect these waves. The transducers are provided with electric leads 2 and fixed in holders *3* and *4*.

In the variant marked "A" the two transducers *1* are located in the polymerizing medium, inside the reactor vessel *7*, equipped with a radial propeller *8* in the other variant, i.e. alternative "B", only one transducer *1* is located in the reaction vessel *7* while the second transducer *1* is mounted on the outer wall of the vessel *7*. In both cases the transducers *1* are acoustically coupled with ultrasonic delay lines *5*, which together with holders *3* and *4* form part of the pressure and electric insulation jacket *6*.

The apparatus for continuous measuring of the changes in rheological properties of monomers, such as vinyl chloride, during the polymerization process, in the variant according to the invention, operates as follows: the apparatus is put into the vessel 7 of the polymerization reactor in such a way that either both the ultrasonic probes, i.e. the probes of the transducer 1, or at least one of them is completely immersed in the polymerizing system, e.g. vinyl chloride, in the carrier medium.

Fed into the transmitting transducer are radio-frequency pulses of the carrier frequency equal to one of the harmonic frequencies of the ultrasonic transducer 1, in the simplest case in the form of quasimonochromatic pulses, e.g. of a frequency of 0.35 MHz and a pulse length of 15 μs, with their damping and possibly also the rate of propagation during the passage through the polymerizing vinyl chloride measured in dependence on polymerization time.

The length, repetition rate and amplitude of rf pulses are chosen such that the radiated power of longitudinal ultrasonic waves transmitted into the polymerizing system and its carrier medium does not affect the course of polymerization.

The measured values of absorption or of the rate of propagation of longitudinal ultrasonic waves are compared with the values of model polymerization or they are further processed in electronic circuits to be used for feedback control of the process, for indicating emergency conditions, etc. The measuring and recording of absorption and rate of propagation of ultrasonic signals can be carried out by well-known methods of physical acoustics and electronics.

Analogously, th measurement is carried out also for other frequencies of longitudinal

ultrasonic waves for the identical polymerization cycle with the result that the spectral dependence f the quantities measured and the optimum valu of the frequency measured are obtained.

With the aid of more sophisticated electronic and ultrasonic equipment it is also possible to introduce into the polymerizing system longitudinal ultrasonic oscilations in the form of videopulses, which having passed through the polymerizing medium are scanned while a rapid spectral and amplitude analysis is simultaneously carried out.

The method according to the present invention can of course be applied also to measuring changes in rheological volume properties of other monomers during their polymerization; it can be applied with all types of polymerization such as emulsion, solution or precipitation, stereospecific and partially also bulk polymerizations.

CLAIMS

1. A method of continuous measurement of changes in rheological properties of monomers during a polymerization process, comprising introducing into the polymerizing system longitudinal ultrasonic oscillations of a frequency of 0.02 to 100 MHz, with the absorption or the rate of propagation of these oscillations being scanned during the polymerization process.

2. Apparatus to carry out the method according to claim 1, including at least one ultrasonic transducer which is adapted for both generating and receiving longitudinal ultrasonic waves and which is acoustically coupled with ultrasonic delay lines located in the polymerizing system.

3. Apparatus according to claim 2, wherein ultrasonic transducers are provided, one of which is adapted for generating and the other for receiving longitudinal ultrasonic waves, while both transducers are acoustically coupled with their own ultrasonic delay lines.

4. Apparatus according to claim 3, wherein the two ultrasonic transducers being located in the polymerizing monomer.

5. Apparatus according to claim 3, wherein one of the ultrasonic transducers is located in the polymerizing monomer and the other outside the reaction vessel, the latter being acoustically coupled with the polymerizing monomer.

6. Apparatus according to claim 5, wherein the latter transducer is coupled with the polymerizing monomer via the jacket of the vessel.

7. Apparatus according to any one of claims 2 to 6, wherein the ultrasonic transducer or transducers are located in holders, which together with delay lines form the pressure and electric insulation jacket of the transducer.

8. A method of continuous measurement of changes in rheological properties of monomers during a polymerization process as claimed in claim 1, and substantially as hereinbefore described.

9. Apparatus for continuously measuring changes in rheological properties of monomers during a polymerizing process substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.

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